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(54) Laundry detergent substrate articles.

(57) Substrate articles, containing mixtures of cationic and nonionic surfactants, which yield excellent removal of particulate and greasy/oily soils from fabrics, and wherein the detergent components are rapidly and completely released into the laundry solution, are disclosed. Preferred articles additionally contain selected materials which minimize the bleeding of the surfactant components through the substrate sheets. A method of laundering fabrics using these articles is also disclosed.

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LAUNDRY DETERGENT SUBSTRATE ARTICLES

The present invention relates to laundry substrate articles, yielding excellent removal of particulate and greasy/oily soils, which contain mixtures of specific types of nonionic and cationic surfactants. These articles are formulated so as to increase the rate at which the nonionic/cationic surfactant mixture is released into the washing solution, thereby maximizing the cleaning benefit obtained.

The convenience and efficiency which is obtained by incorporating premeasured amounts of laundry detergent compositions into substrate articles, for direct addition to the automatic washing machine, are well known. Examples of such articles are taught in U.S. Patent No. 4095946, Jones et al, filed March 25, 1977; U.S. Patent No. 4118525, Jones, filed March 25, 1977; and U.S. Patent No. 4113630, Hagner et al, filed March 25, 1977, all of the disclosures of which are incorporated herein by reference. In addition, European Patent Application Nos. 78 200 065.7 and 78 200 064.0 both of which are incorporated herein by reference, disclose detergent compositions, containing mixtures of specifically defined nonionic and cationic surfactants, which yield outstanding removal of particulate and greasy/oily soils. It would be very desirable to combine the outstanding cleaning performance of these detergent compositions with the

convenience of the substrate articles.

In order to combine these two technologies, several problems must be overcome. It is necessary to provide for rapid and complete release of the surfactant mixture from the substrate into the laundry solution, in order both to maximize the cleaning benefits obtained during the relatively short automatic laundering cycle, and to minimize waste of the surfactant components. Further, it is desirable to minimize the bleeding of the surfactant mixture, particularly the nonionic component, through the substrate sheets, which may occur during storage of the articles. It has now been found that the release of the nonionic/cationic surfactant mixtures into the laundry solution can be greatly increased by using the specific types of solubilization aids defined herein. It has further been found that the bleeding of the detergent components can be controlled by including the specific materials, having the required particle sizes, disclosed herein in the substrate articles.

It is, therefore, an object of the present invention to define a laundry substrate article providing excellent cleaning and which may also provide fabric care benefits, such as static control, fabric softening, and dye transfer inhibition, to the laundered fabrics.

It is another object of the present invention to provide a substrate article having improved release of its active components into the wash solution.

It is a further object of the present invention to provide a laundry substrate article wherein the bleeding of active components through the substrate sheets is minimized but which also exhibits proper release of the active components into the washing solution.

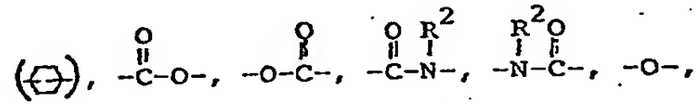
It is yet another object of the present invention to provide a process for laundering fabrics using the substrate articles described herein.

The present invention relates to substrate articles, used in the laundering of fabrics, which exhibit improved release of their active components into the washing solution, and which consist essentially of a water-insoluble, wet-strength substrate, carrying an effective amount of a detergent composition comprising:

(a) from about 5 to about 95% of a surfactant mixture consisting essentially of:

(i) a nonionic surfactant having an HLB of from about 5 to about 17; and

(ii) a cationic surfactant having the formula $R^1_m R^2_x Y_L Z$, wherein each R^1 is an organic group containing a straight or branched alkyl or alkenyl group optionally substituted with up to 3 phenyl groups and, optionally, interrupted by up to 4 structures each of which is selected from the group consisting of



and mixtures thereof, and which contain from about 8 to about 22 carbon atoms, and which may additionally contain up to 20 ethoxy groups, m is a number of from 1 to 7 and no more than one R^1 can have more than 12 carbon atoms when m is 3 or greater, each R^2 is an alkyl or hydroxy alkyl group containing from 1 to 4 carbon atoms or a benzyl group with no more than one R^2 in a molecule being benzyl, x is a number from 0 to 7, the remainder of any carbon, nitrogen, sulfur or phosphorus atom positions being filled by hydrogens, Y is selected from the group consisting of:

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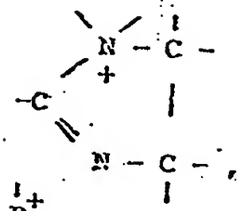
(2) 

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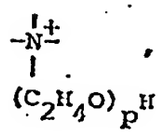
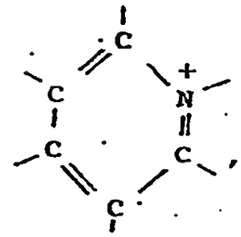
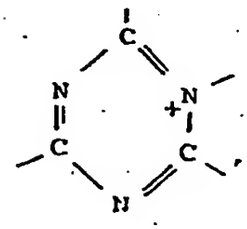
(5)  , wherein p is from 1 to 20,

(6) 

(7)  , and

(8) mixtures thereof.

L is a number of from 1 to 3, Z is an anion in a number sufficient to give electrical neutrality, said cationic surfactant being at least water-dispersible in admixture with said nonionic surfactant; the ratio of said nonionic surfactant to said cationic surfactant being in the range of from about 5 : 3 to about 300 : 1;

(b) from about 1% to about 30% of a nonionic or cationic solubilization aid which has a solubility of 100°F water of at least about 20% by weight, and which completely dissolves in 100°F water in no more than about 2 minutes.

Preferred nonionic surfactants are those having the formula $R(OC_2H_4)_nOH$, wherein R is a primary or secondary alkyl chain of from about 8 to 22 carbon atoms and n is an average of from about 2 to about 9.

Preferred articles additionally contain, in the detergent composition, from about 2 to about 20% of a thickening material having an average particle size of no greater than about 3.0 microns, selected from the group consisting of clays, silicas, amides, soaps, and mixtures thereof. These preferred articles exhibit improved release of their active components into the laundry solution, while also minimizing undesirable bleeding of those active components through the substrate sheets. The articles herein may also contain various optional adjunct materials commonly employed in laundry detergent compositions.

A method of laundering fabrics, utilizing the articles of the present invention, is also taught herein.

Detailed Description of the Invention

Substrate Component

The articles of the present invention comprise a water-insoluble, wet-strength substrate carrying an effective amount of a detergent composition, further defined herein. The exact amount of the detergent composition carried by the substrate depends upon the particular substrate materials and active materials included in the composition. Preferred articles carry from about 3 to 120, preferably from about 20 to 80, grams of the detergent composition. The detergent composition may be loaded onto the substrate material in any of the ways conventionally known in the art, such as coating or impregnation. Particularly preferred substrates are sandwich-type articles in which at least one of the substrate sheets used has an air permeability of at least about 10 cubic feet per minute per square foot.

The substrates employed herein are water-insoluble and are solid or substantially solid materials. They can be dense or open in structure, preferably the latter. Examples of suitable materials which can be used as a substrate herein include, among others, water-insoluble particulate materials (such as certain silicas, silicon dioxide, clays, and aluminosilicates), foam, foil, sponge, paper, woven cloth, and nonwoven cloth. The term "cloth", as used herein, means a woven or nonwoven fabric or cloth used as a substrate, in order to distinguish it from the term "fabric" which means the textile fabric which is desired to be laundered. Absorbent capacity, thickness, or fiber density are

not limitations on the substrates which can be used herein, as long as the substrates exhibit sufficient wet-strength so as to maintain their structural integrity through the complete washing and drying cycles in which they are used. Further, the substrates must have certain thermal stability characteristics, i.e., they should not have a melting point or ignite at temperatures below 300°F, preferably about 425°F, in order to permit their use in automatic clothes dryers. Preferably, the substrates employed herein are wet-strength paper or nonwoven cloth.

Paper substrates which can be employed herein encompass the broad spectrum of known paper structures and are not limited to any specific papermaking fiber or wood pulp. Thus, the fibers derived from soft woods, hard woods, or annual plants (e.g., bagasse, cereal straw, and the like), and wood pulps, such as bleached or unbleached kraft, sulfite, soda ground wood, or mixtures thereof, can be used. Moreover, the paper substrates which can be employed herein are not limited to specific types of paper, as long as the paper exhibits the necessary wet-strength and thermal stability.

A specific example of a paper substrate preferred herein is a two-ply paper having a basis weight of about 50 lbs. per 2,880 sq. ft. made from, for example, a mixture of ground wood and kraft-bleached wood pulps. Another example is the absorbent, multi-ply toweling paper particularly preferred in U.S. Patent 3,686,025, Morton, issued August 22, 1972 and disclosed in U.S. Patent 3,414,459, Wells, said patents being incorporated herein by reference.

The preferred nonwoven cloth substrates used in the invention herein can generally be defined as adhesively bonded fiberous products, having a web or corded fiber structure (where the fiber strength is suitable to allow carding) or comprising fiberous mats, in which the fibers are distributed haphazardly or in a random array (i.e., an array of fibers in a carded web wherein partial orientation of the fibers is frequently present as well as a completely haphazard distributional orientation) or substantially aligned. The fibers can be natural (e.g., wool,silk, jute, hemp, cotton, linen, sisal, or ramie) or synthetic (e.g., rayon, cellulose ester, polyvinyl derivatives, polyolefins, polyamides, or polyesters). Any diameter or denier of the fiber, generally up to about 10 denier, can be used in the present invention.

The substrates which are used in the detergent articles herein, can take a variety of forms. For example, the substrate can be in the form of a particulate solid, pad, ball or puff or it can be a sheet or swatch of woven or nonwoven cloth. When the substrate is paper or nonwoven, individual sheets of desired length and width can be used, or a continuous roll of desired width from which a measured length is torn off, may be employed.

The detergent composition carried by this substrate comprises from about 5 to about 95%, preferably from about 10 to about 90%, and most preferably from about 15 to about 85%, of a mixture of specifically defined nonionic and cationic surfactants. The ratio of nonionic surfactant to cationic surfactant used in these mixtures is in the range of from about 5 : 3 to about 300 : 1, preferably from about 5 : 3 to about 100 : 1, most preferably from about 5 : 3 to about 50 : 1. Particularly preferred ratios are from about 5 : 3 to about 10 : 1, preferably from about 5 : 3 to 5 : 1, particularly about 5 : 2.

Nonionic Surfactant

Conventional nonionic surfactants, well known in the detergency arts, and preferably those having HLB's from about 5 to about 17, may be used in the articles of the present invention. These surfactants may be included either singly or in mixtures, and are preferably used in combination with the preferred alcohol exthoxylate nonionic surfactants, described hereinafter. Examples of such surfactants are listed in U.S. Patent 3,717,630, Booth, issued February 20, 1973, and U.S. Patent 3,332,880, Kessler et al, issued July 25, 1967, each of which is incorporated herein by reference. Non-limiting examples of suitable nonionic surfactants which may be used in the present invention include the polyethylene oxide condensates of alkyl phenols, the condensation products of straight or branched primary or secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, the condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol, and the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and propylene diamine.

Preferred nonionic surfactants used in the compositions of the present invention are biodegradable and have the formula $R(OC_2H_4)_nOH$, wherein R is a primary or secondary alkyl chain of from about 8 to 22, preferably from about 10 to 20, carbon atoms, and n is an average of about 2 to about 9. The surfactants have an HLB (hydrophilic-lipophilic balance) of from about 5 to about 17, preferably from about 6 to about 15. HLB is defined in detail in Nonionic Surfactants, by M. J. Schick, Marcel Dekker, Inc., 1966, pages 607-613, incorporated herein by reference. In preferred nonionic surfactants, n is from 4 to 7.

Particularly preferred nonionic surfactants for use in the articles of the present invention include the condensation product of C_{10} alcohol with 3 moles of ethylene oxide; the condensation product of tallow alcohol with 9 moles of ethylene oxide; the condensation product of coconut alcohol with 5 moles of ethylene oxide; the condensation product of coconut alcohol with 6 moles of ethylene oxide; the condensation product of C_{12-13} with 6.5 moles of ethylene oxide, and the same condensation product which is stripped so as to remove substantially all lower ethoxylate and non-ethoxylated fractions; the condensation product of C_{12-13} alcohol with 3 moles of ethylene oxide which is stripped so as to remove the lower ethoxylate and nonethoxylated fractions; the condensation product of C_{14-15} alcohol with 2.25 moles of ethylene oxide; and the condensation product of C_{14-15} alcohol with 7 moles of ethylene oxide.

Where the present invention contains a mixture of a preferred alcohol ethoxylate nonionic surfactant (or surfactants) together with other types of nonionic

surfactants, the ratio of the preferred surfactant (or surfactants) to the remaining nonionic surfactants is preferably within the range of from about 1 : 1 to about 5 : 1. Specific examples of surfactant mixtures useful in the present invention include a mixture of the condensation product of C_{14-15} alcohol with 3 moles of ethylene oxide (Neodol 45-3) and the condensation product of C_{14-15} alcohol with 9 moles of ethylene oxide (Neodol 45-9), in a ratio of lower ethoxylate nonionic to higher ethoxylate nonionic of from about 1 : 1 to about 3 : 1; a mixture of the condensation product of C_{10} alcohol with 3 moles of ethylene oxide together with the condensation product of a secondary C_{15} alcohol with 9 moles of ethylene oxide (Tergitol 15-S-9), in a ratio of lower ethoxylate nonionic to higher ethoxylate nonionic from about 1 : 1 to about 4 : 1; a mixture of Neodol 45-3 and Tergitol 15-S-9, in a ratio of lower ethoxylate nonionic to higher ethoxylate nonionic of from about 1 : 1 to about 3 ; 1; and a mixture of Neodol 45-3 with the condensation product of myristyl alcohol with 10 moles of ethylene oxide, in a ratio of lower ethoxylate to higher ethoxylate of from about 1 : 1 to about 3 : 1.

Preferred nonionic surfactant mixtures contain alkyl glyceryl ether compounds together with the preferred alcohol ethoxylate nonionic surfactants. Particularly preferred are glyceryl ethers having the formula

$$R\text{-}O(CH_2CH_2O)_n\underset{\underset{OH}{|}}{CH_2}CHCH_2OH$$

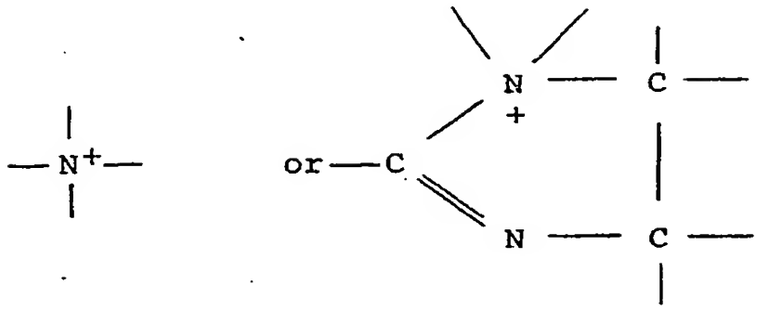
wherein R is an alkyl or alkenyl group of from about 8 to about 18, preferably about 8 to 12, carbon atoms

or an alkaryl group having from about 5 to 14 carbons in the alkyl chain, and n is from 0 to about 6, together with one of the preferred alcohol ethoxylate nonionic surfactants, defined above, in a ratio of alcohol ethoxylate to glyceryl ether from about 1 : 1 to about 4 : 1, particularly about 7 : 3. Glyceryl ethers of the type useful in the present invention are disclosed in Belgian Patent No. 849807 and U.S. Patent No. 4098713.

Cationic Surfactant

The cationic surfactants used in the detergent compositions incorporated into the substrate articles of the present invention have the formula defined above. The specific cationic component to be included in a given system depends to a large extent upon the particular nonionic component to be included in the system, and is selected such that it is at least water-dispersible, or preferably water-soluble, when mixed with said nonionic surfactant. The term "water-dispensible" means that the cationic and nonionic surfactants, as well as any anionic components included in the composition, remain dispersed throughout the laundry solution during the washing process. Mixtures of the above defined cationic materials may also be used in the compositions of the present invention. Small amounts of other cationic materials can be tolerated in such mixtures.

In preferred cationic materials, L is equal to 1 and Y is



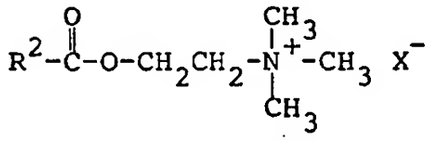
or mixtures thereof. However, L may be greater than 1, such as in cationic components containing 2 or 3 cationic charge centers. Other cationic materials which are useful in the compositions of the present invention include phosphonium, and sulfonium materials.

Where m is equal to 1, it is preferred that x is equal to 3 and R^2 is a methyl group. Preferred compositions of this mono-long chain type include those in which R^1 is a C_{10} to C_{20} alkyl group. Particularly preferred compositions of this class include C_{12} alkyl trimethylammonium halide and C_{14} alkyl trimethylammonium halide.

In order to be sufficiently water-soluble or water-dispersible, the cationic surfactant must satisfy the following chain-length criteria. Where m is equal to 3 or greater, only one of the R^1 chains can be greater than 12 carbon atoms in length. In this instance, it is preferred that x is equal to 1 and that R^2 is a methyl group. In these compositions it is preferred that R^1 is a C_8 to C_{11} alkyl group. Particularly preferred tri-long chain cationics include trioctylmethylammonium halide, and tridecylmethylammonium halide.

A particularly preferred type of cationic

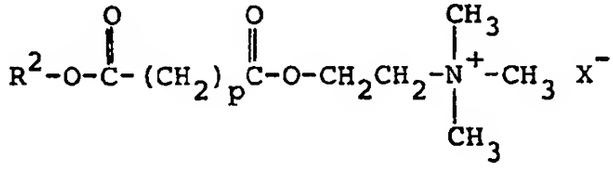
component, is described in Japanese Patent Application 53-79228, filed June 29, 1978, incorporated herein by reference. Particularly preferred cationic surfactants of this type are the choline ester derivatives having the following formula

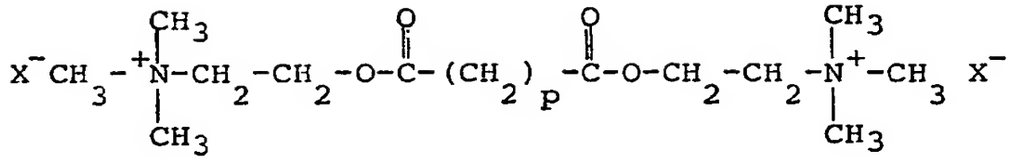


wherein R^2 is C_5 to C_{30} straight or branched chain alkyl or alkenyl or akylphenyl, as well as those wherein the ester linkage in the above formula is replaced with a reverse ester, amide or reverse amide linkage.

Particularly preferred examples of this type of cationic surfactant include stearoyl choline ester quaternary ammonium halides (R^2 = C_{17} alkyl), palmitoyl choline ester quaternary ammonium halides (R^2 = C_{15} alkyl), myristoyl choline ester quaternary ammonium halides (R^2 = C_{13} alkyl), lauroyl choline ester ammonium halides (R^2 = C_{11} alkyl), and tallowyl choline ester quaternary ammonium halides (R^2 = C_{15}-C_{17} alkyl).

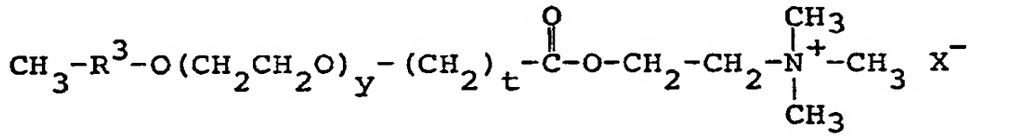
Additional preferred cationic components of the choline ester variety are given by the structural formulas below, wherein p may be from 0 to 20.

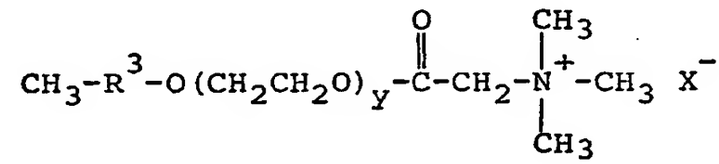




In addition to the advantages of the other cationic surfactants disclosed herein, the choline ester type of cationic component is environmentally desirable, when its R^2 chain is not highly branched, since it is biodegradable, yielding environmentally acceptable compounds, both in terms of its long alkyl chain and its nitrogen-containing segment.

Another type of preferred biodegradable cationic surfactant for use in the articles of the present invention is disclosed in Japanese Patent Application No. 53-79227 incorporated herein by reference. Preferred embodiments of this type are choline esters, particular formulas of which are given below, in which t is 0 or 1, y is from 1 to 20, R^3 is C_1 to C_{20} alkyl or alkenyl and X is an anion which makes the compound at least water-dispersible, preferably chloride, bromide or iodide.





The above types of preferred surfactants, when used in the compositions of the present invention, yield excellent particulate soil, body soil, and greasy/oily soil removal. In addition, the detergent compositions control static and soften the fabrics laundered therewith, and inhibit the transfer of certain dyes in the washing solution. Further, these cationic surfactants are environmentally desirable, as long as the molecules do not contain highly branched segments, since both their long chain alkyl segments and their nitrogen segments are biodegradable, in that they degrade to yield environmentally acceptable compounds. Where this type of biodegradable cationic surfactant is used, it is preferred that the detergent compositions have a pH of not greater than about 11, preferably less than about 10, in the laundry solution, in order to minimize hydrolysis of the cationic surfactant.

Solubilization Aid

The compositions used in the articles of the present invention additionally contain from about 1 to about 30% preferably from about 3 to about 25%, and most preferably from about 5 to about 20%, of specifically selected solubilization aid components. These components should be nonionic or cationic in nature, in order to be compatible with the nonionic/cationic surfactant mixture, and must have a solubility in 100°F water of at least about 20%, and preferably at least about 25%, by weight. In addition, the solubilization components must be selected such that they completely dissolve in 100°F water in no more than about 2 minutes, and preferably no more than about 1 minute. In order to achieve the proper release of the active components from the substrate carrier, it is necessary that the

solubilization aid which is chosen satisfy both of the above solubility criteria. Thus, sodium chloride, which is highly soluble, thereby satisfying the first criterion, does not have a sufficiently rapid rate of solubility to satisfy the second criterion, and therefore it is not satisfactory for use in the articles of the present invention.

Although not wishing to be bound by theory, it is believed that as the solubilization component rapidly dissolves in the laundry solution, the surface area at the interface between the laundry solution and the cationic/nonionic surfactant mixture is increased, thus enhancing the dissolution of the mixture from the substrate into the washing system. Preferred solubilization aids are those selected from the group consisting of choline chloride, ammonium chloride, phenylmethylammonium chloride, sucrose, glucose, polyethylene glycol having a molecular weight of from about 1,000 to about 6,000, preferably about 4,000, and mixtures of those materials. Particularly preferred solubilization materials are choline chloride, sucrose, glucose, polyethylene glycol having a molecular weight of from about 1,000 to about 6,000, preferably about 4,000, and mixtures thereof. Solubilization aids which satisfy the above solubility criteria and, in addition, are hygroscopic, such as choline chloride, are particularly preferred for use in the articles of the present invention.

Preferred detergent compositions used in the substrate articles of the present invention additionally contain from about 2 to about 20%, preferably from about 5 to about 17%, and most preferably from about 5 to about 15%, of a clay, silica, amide or soap material having an average particle size of no greater than about 3.0 microns. Preferred components

are silicas, clays, and mixtures of those materials. It has been found that when these materials, having the particle sizes stated herein, are included in the detergent compositions used in the present invention, the undesirable bleeding of the active components through the substrate materials, during storage, is minimized. It is advantageous to minimize such bleeding, since it may result in a loss of active material, as well as appearance and handling negatives to the user. Preferred anti-bleeding materials are those having an average particle size of no greater than about 2.5 microns, most preferably no greater than about 2 microns. Particularly preferred materials of this type include Zeosyl 200, a silica material having an average agglomerated particle size of about 2 microns, commercially available from J. M. Huber Corporation; Bentone 27, a bentonite clay material having an average particle size of about 0.8 microns, commercially available from N. L. Industries; Quso G30, a silicate material having an average particle size of about 1 to 2 microns and a surface area of about 300 sq.m./g., commercially available from Philadelphia Quartz Company; and mixtures of these materials. Sodium stearate and ammonium stearate are examples of soaps useful as anti-bleeding agents in the present invention, while myristamide and behenamide are examples of amides which may be used. It is necessary that when these thickener materials are used in the articles of the present invention, that they be included together with the solubilization aids, defined above, in order to have sufficiently rapid release of the thickened detergent composition into the laundry solution.

In particularly preferred embodiments of the present invention, the detergent composition contained in the

article additionally contains from about 2 to about 25%, preferably from about 2 to about 16%, and most preferably from about 3 to about 10% of a fatty amide surfactant. In relation to the nonionic/cationic surfactant system, the ratio of the cationic/nonionic mixture to the amide component in the composition is in the range of from about 5 : 1 to about 50 : 1, preferably from about 8 : 1 to about 25 : 1. The addition of the amide component results in excellent particulate soil removal performance, as well as improved soil antiredeposition characteristics, and the development is described in European Patent Application 78 200 067.3.

The compositions of the present invention may also contain additional ingredients generally found in laundry detergent compositions, at their conventional art-established levels, as long as these ingredients are compatible with the nonionic and cationic components. For example, the compositions may contain up to about 15%, preferably up to about 5%, and most preferably from about 0.1% to about 2% of a suds suppressor component. Typical suds suppressors include long chain fatty acids, such as those described in U.S. Patent 2,954,347, issued September 27, 1960, St. John, and combinations of certain nonionics therewith as disclosed in U.S. Patent 2,954,348, issued September 27, 1960, Schwoeppe, both disclosures being incorporated herein by reference. Other suds suppressor components useful in the compositions of the present invention include the silicone suds controlling agents described in U.S. Patent 3,933,679, the self-emulsifying silicone suds suppressors described in Belgian Patent 847268, the microcrystalline waxes described in U.S. Patent 4,056,481, and alkyl phosphate esters such as monostearyl phosphate and monooleyl phosphate.

Other adjunct components which may be included in the articles of the present invention, in their convention art-established levels for use (i.e., from 0 to about 40%), include anionic, zwitterionic and ampholytic cosurfactants, detergency builders, bleaching agents, bleach activators, soil-suspending agents, corrosion inhibitors, dyes, fillers, optical brighteners, germicides, pH adjusting agents, enzymes, enzyme-stabilizing agents, perfumes, fabric softening components, static control agents, and the like. However, because of the numerous and diverse performance advantages of the articles of the present invention, certain types of components, such as detergency builders, static control agents, fabric softening agents and germicides, may not be necessary in a particular formulation.

Examples of cosurfactants and detergency builders, which may be used in the compositions of the present invention, are found in U.S. Patent 3,717,630, Booth, issued February 20, 1973, and Japanese Patent Application No. 53-79227, both of which are incorporated herein by reference. However, these components, particularly anionic surfactants, should be checked with the particular cationic/nonionic surfactant system used, in order to ascertain whether they are compatible.

The use of the substrate articles of the present invention provides a convenient and efficient method whereby soiled fabrics may be cleaned. The substrate article (or articles) is placed in an automatic washing machine together with the fabrics

to be laundered, preferably at the start of the washing cycle, and is allowed to remain there until the washing cycle is completed. During this process, which includes the agitation of the laundry solution, the surface-active compositions and the other fabric conditioning components which are contained in the substrate article are rapidly and completely released into the washing solution and provide cleaning and other benefits to the fabrics washed therein. If the substrate article additionally contains any dryer-activated fabric conditioning components, such as those described in U.S. Patent Nos. 4095946 and 4113630 both of which are incorporated herein by reference, the washed fabrics and the substrate article are placed in an automatic dryer, where they are subjected to the heated drying cycle. In the course of this drying operation, the dryer-activated fabric conditioning components are released, providing additional benefits to the laundered fabrics.

All percentages, parts, and ratios used herein are by weight unless otherwise specified.

The following nonlimiting examples illustrate the compositions and method of the present invention.

EXAMPLE I

The ability of various substrate articles to release active components into a laundry solution was tested in the following manner. Detergent compositions, having the formulations stated below, were prepared by mixing together the ingredients in the proportions given.

Composition	Components	Weight %
A	$C_{17}H_{35}-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_2-\underset{\underset{\displaystyle CH_3}{\|}}{\overset{\overset{\displaystyle CH_3}{\|}}{N^+}}-CH_3\ Cl^-$	26.6
	Condensation product of coconut alcohol with 5 moles of ethylene oxide	52.5
	Ammonia amide	7.4
	Borax · 10 H_2O	13.5
B	Same as A, above, plus Choline chloride (6.4 grams)	~10%
C	Same as A, above, plus Choline chloride (9.6 grams)	~13%
D	Same as A, above, plus Zeosyl 200 (3.4 grams)	~ 5%
E	Same as A, above, plus Zeosyl 200 (3.4 grams) Choline chloride (7.1 grams)	 ~4.5% ~9.5%
F	Same as A, above, plus Bentone 27 (10.1 grams)	~13.5%
G	Same as A, above, plus Bentone 27 (10.1 grams) Choline chloride (7.5 grams)	 ~12% ~ 9%

Detergent articles were made with each of these compositions by spreading about 65 grams of the composition on one side of an 8" x 11" sheet of a Scott 8050 Industrial Towel, having an air permeability of about 130 cu. ft./min./sq. ft., a basis weight of about 77.5 grams per square yard,

and a thickness of 44 mils. An identical sheet of the paper towel was placed on top of the coated side of the original sheet, and the edges were sewn together so as to enclose the composition within the article. Pairs of the articles were then placed in a Kenmore automatic washing machine together with a 5-1/2 to 6 pound mixed fabric load. The washer was run through a gentle agitation wash cycle, using 22 gallons of 80°F water (Cincinnati city water--8-10 grains per gallon of mixed hardness), with a cold water rinse. At the conclusion of the washing operation, the substrate articles were removed and the amount of active material released from the article was visually estimated. The table below summarizes the data obtained.

Run	Compositions	% Active Dissolved from Article (Visually Estimated)
I	A	20%
	B	95%
II	A	10%
	C	95%
III	D	10%
	E	80%
IV	F	10%
	G	80%

These data demonstrate the dramatic increase in the rate and completeness of release of the detergent composition from the substrate article, obtained where the solubilization aids of the present invention are used.

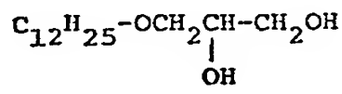
Substantially similar component release results are obtained where the choline chloride solubilization aid, in the above formulations, is replaced, in whole or in part, by equivalent amounts of ammonium chloride, phenyl methyl ammonium chloride, sucrose, glucose, polyethylene glycol having a molecular weight of from about 1,000 to about 6,000, particularly about 4,000, or mixtures of those components.

Similar results are also obtained where the nonionic component, used above, is replaced by the condensation product of C_{10} alcohol with three moles of ethylene oxide, the condensation product of coconut alcohol with six moles of ethylene oxide, the condensation product of coconut alcohol with seven moles of ethylene oxide, the condensation product of C_{12-13} alcohol with 6.5 moles of ethylene oxide, the condensation product of C_{14-15} alcohol with seven moles of ethylene oxide, or the condensation product of C_{12-13} alcohol with three moles of ethylene oxide stripped so as to remove the lower ethoxylate and unethoxylated fractions.

Excellent results are also obtained where the detergent compositions used contain nonionic to cationic surfactant ratios of about 100:1, 70:1, 50:1, 35:1, 25:1, 20:1, 15:1, 10:1, 5:1, 4:1, 3:1, 20:7, 20:9, 2:1, or 5:3.

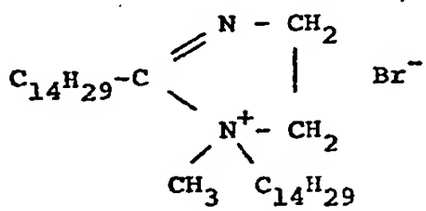
Similar results are also obtained where the nonionic component is replaced by a mixture of the condensation product of C_{14-15} alcohol with three moles of ethylene oxide together with the condensation product of C_{14-15} alcohol with seven moles of ethylene oxide, having a ratio of lower ethoxylate nonionic to higher ethoxylate nonionic of about 2:1; a mixture of the condensation product of C_{14-15} alcohol

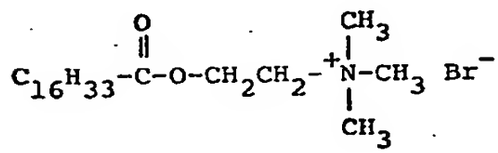
with 3 moles of ethylene oxide together with the condensation product of myristyl alcohol with 10 moles of ethylene oxide, in a ratio of lower ethoxylate nonionic to higher ethoxylate nonionic of about 1:1; or a mixture of the condensation product of coconut alcohol with five moles of ethylene oxide together with an alkyl glyceryl ether having the formula:

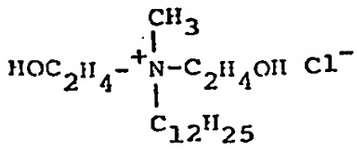


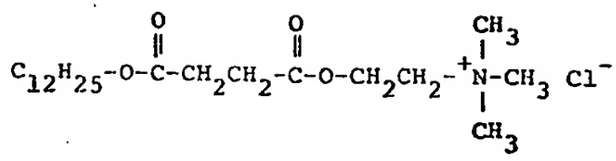
in a ratio of alcohol ethoxylate to glyceryl ether of about 7:3.

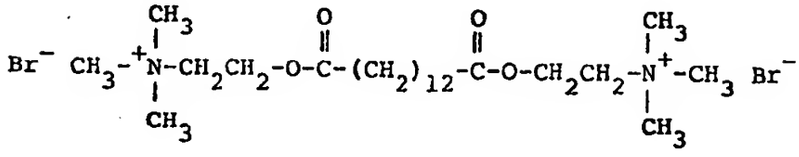
Substantially similar release results are also obtained where the cationic component is replaced by C_{12} trimethylammonium chloride, C_{14} trimethylammonium bromide, di-C_{10} dimethylammonium bromide, di-C_{12} dimethylammonium chloride, tri-C_8 methylammonium bromide, tri-C_{10} methylammonium chloride, or cationic components having the following formulae:

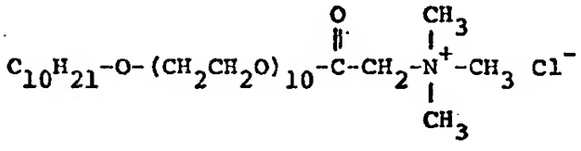












EXAMPLE II

Using the compositions given below, included in the substrate articles in the amounts specified, the release characteristics of several articles of the present invention were examined, using the method and article structure described in Example I, above. The percentage of the total detergent composition released into the laundry solution was calculated by weighing the substrate article before adding it to the washing machine, and then reweighing after it had been used in the washing cycle and dried. The data obtained are summarized in the table below.

Composition	Component	grams/article	Weight %	% Active Released from Article
A	$C_{17}H_{35}-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2-\overset{CH_3}{\overset{\|}{\overset{+}{N}}}-CH_3$ Cl^- (with CH_3 below N)	13.8	20.4	79.4
	Condensation product of coconut alcohol with 5 moles of ethylene oxide	29.8	43.6	
	Ammonia amide	4.2	6.1	
	Borax · 5 H_2O	6.0	8.8	
	Brightener (anionic)	0.8	1.2	
	Zeosyl 200	6.7	9.9	
	Choline chloride	6.8	10.0	
B	Same as A, above, except			95.7
	Zeosyl 200	6.7	8.8	
	Choline chloride	15.3	20.0	
C	Same as A, above, except			70.8
	Zeosyl 200	4.2	6.4	
	Choline chloride	6.5	10.0	
D	Same as A, above, except			92.0
	Zeosyl 200	4.2	5.7	
	Choline chloride	14.7	20.0	

These data demonstrate the excellent release of detergent components into the laundry solution obtained using the substrate articles of the present invention.

EXAMPLE III

Using the procedure and article structure described in Example I, above, the release of detergent components from the articles, given below, was determined. After the laundering process was completed, the percentage of the active components released from the substrate article was visually estimated, and the results are summarized in the table below.

Composition	Component	grams/article	Weight %	% Active Released from Article
A	$C_{17}H_{35}-\overset{O}{\overset{\|\|}{C}}-O-CH_2CH_2-\overset{CH_3}{\overset{\|}{\overset{+}{N}}}-CH_3\ Cl^-$ (with CH_3 below N)	13.8	28.9	20
	Condensation product of coconut alcohol with 5 moles of ethylene oxide	29.8	62.5	
	Brightener (anionic)	0.8	1.7	
	Zeosyl 200	3.3	6.9	
	Choline chloride	-	-	
B	Same as A, above, except			90
	Zeosyl 200	3.3	6.2	
	Choline chloride	5.3	10.0	
C	Same as A, above, except			75
	Zeosyl 200	3.3	5.5	
	Choline chloride	11.9	20.0	

These data demonstrate the excellent release results obtained using the articles of the present invention, as well as the necessity of using the solubilization aids described herein when the articles of the present invention contain components for the minimization of component bleeding.

EXAMPLE IV

The bleeding characteristics of the active components of substrate articles, described below, were tested in the following manner. Detergent compositions having the basic formula given below, but containing various types of anti-bleeding components, were formulated by mixing together the components in the proportions specified. The anti-bleeding materials tested were Zeosyl 200, a silica material having an average agglomerated particle size of about 2 microns; Bentone 27, a bentonite clay material having an average particle size of 0.8 microns; Quso G30, a silicate material having an average particle size of about 1 to 2 microns; and Zeolite A, a sodium aluminosilicate material having an average particle size of about 4 microns.

Component	Wt. %	grams/ article
$C_{17}H_{35}-\overset{O}{\overset{\parallel}{C}}-O-CH_2CH_2-\overset{+}{N}(CH_3)_3\ Cl^-$	20.4	11.9
Condensation product of coconut alcohol with 5 moles of ethylene oxide	50.9	29.8
Brightener (anionic)	1.4	0.8
Ammonia amide	7.1	4.2
Borax · 5 H_2O	10.2	6.0
Anti-Bleeding Component	10.0	5.8

Substrate articles containing each of the above-listed anti-bleeding components were made by coating one side of an 8" x 11" sheet of a Scott 8050 Industrial Towel, having an air permeability of about 130 cu. ft./min./sq. ft., a basis weight of about 77.5 grams per square yard, and a thickness of 44 mils, with about 58.5 grams of a given detergent composition. An identical sheet of the paper towel was placed on top of the coated side of the original sheet and the edges were sewn together so as to enclose the composition within the article.

The bleeding characteristics of each article was determined by simulating the storage of a stack of the articles in a cardboard package. Each substrate was placed on top of a piece of cardboard, and had a 4" square Plexiglass block placed on top of it. A 100 gram weight was placed on the Plexiglass block and the substrate was stored at 80°F/60% relative humidity for a two week period. At the end of this storage period, the diameter of the circle of the nonionic component which bled onto the piece of cardboard was measured. A circle having a diameter of greater than 5 inches is considered to be an indication of excessive bleeding under these test conditions. The data obtained are summarized in the table below.

Thickener	Particle Size (Microns)	Bleeding (Inches)
Zeosyl 200	2.0	4.25
Bentone 27	0.8	3.00
Quso G30	1.0-2.0	4.25
Zeolite A	4.0	5.75

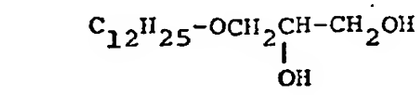
These data demonstrate the advantages, in terms of the minimization of component bleeding, obtained by using the specific types of anti-bleeding agents disclosed in the present application.

Similar results are also obtained where the nonionic component, used above, is replaced, in whole or in part, by the condensation product of C_{10} alcohol with three moles of ethylene oxide, the condensation product of coconut alcohol with six moles of ethylene oxide, the condensation product of coconut alcohol with seven moles of ethylene oxide, the condensation product of C_{12-13} alcohol with 6.5 moles of ethylene oxide, the condensation product of C_{14-15} alcohol with seven moles of ethylene oxide, the condensation product of C_{12-13} alcohol with three moles of ethylene oxide stripped so as to remove the lower ethoxylate and unethoxylated fractions, or mixtures of these surfactants.

Excellent results are also obtained where the detergent compositions included contain nonionic to cationic surfactant ratios of about 100:1, 70:1, 50:1, 40:1, 35:1, 25:1, 15:1, 5:1, 4:1, 10:3, 20:7, 20:9, 2:1, or 5:3.

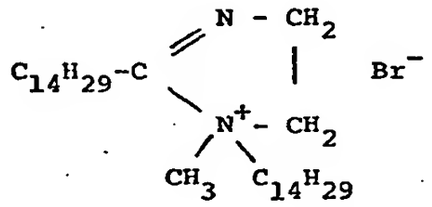
Similar results are also obtained where the nonionic component is replaced by a mixture of the condensation product of C_{14-15} alcohol with three moles of ethylene oxide together with the condensation product of C_{14-15} alcohol with seven moles of ethylene oxide, in a ratio of lower ethoxylate nonionic to higher ethoxylate nonionic of about 2:1; a mixture of the condensation product of C_{14-15} alcohol with 3 moles of ethylene oxide together with the condensation product of myristyl alcohol with 10 moles of ethylene oxide,

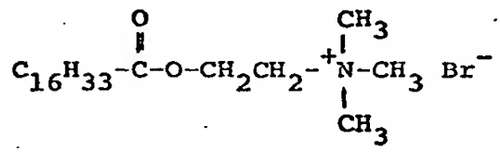
in a ratio of lower ethoxylate nonionic to higher ethoxylate nonionic of about 1:1; or a mixture of the condensation product of coconut alcohol with five moles of ethylene oxide together with an alkyl glyceryl ether having the formula:

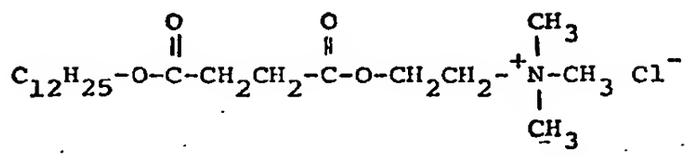


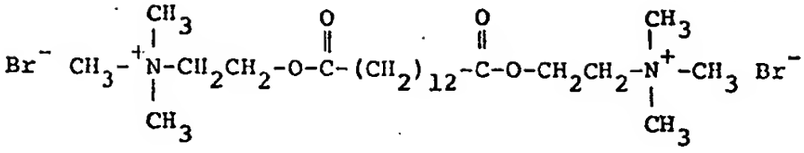
in a ratio of alcohol ethoxylate to glyceryl ether of about 7:3.

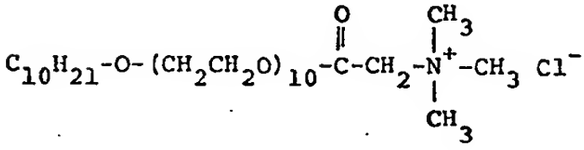
Substantially similar results are also obtained where the cationic component is replaced by C_{12} trimethylammonium chloride, C_{14} trimethylammonium bromide, di-C_{10} dimethylammonium bromide, di-C_{12} dimethylammonium chloride, tri-C_8 methylammonium bromide, tri-C_{10} methylammonium chloride, or cationic components having the following formulae:





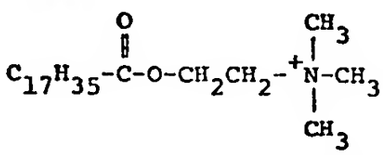






EXAMPLE V

A substrate article, for use in the automatic laundering operation, is made by coating one side of an 8" x 11" sheet of Scott 8050 Industrial Towel with about 50 grams of a composition having the formulation given below. The composition is made by intimately mixing the nonionic and cationic surfactants together, at a temperature of about 80°C, to form a thick paste, and then adding the remaining components.

Component	Wt. %
	25.7
Condensation product of coconut alcohol with 5 moles of ethylene oxide	50.7
Zeosyl 200	9.8
Choline chloride	11.8
Minors (suds suppressor, perfume, brightener, etc.)	balance to 100

An identical sheet of the paper towel is placed on top of the coated side of the original sheet, and the edges are sewn together so as to enclose the composition between the substrate sheets. This article provides a convenient method for introducing the detergent compositions into the laundry solution, and has excellent characteristics in terms of rate of release of the detergent components into the laundry solution and the minimization of component bleeding during storage.

A substrate article may also be made by coating one side of an 11" x 11" sheet of melt-blown polypropylene, having a thickness of about 29 mils, a basis weight of about 58.5 grams/sq. yd., and an air permeability of about 66 cu. ft./min./sq. ft., with about 60 grams of the detergent composition described above, placing an identical substrate sheet over the coated sheet, and heat sealing together the edges of the two substrates, enclosing the detergent composition within the article.

EXAMPLE VI

A laundry detergent substrate article of the present invention, containing the detergent composition given below, is made using the procedure taught in Example V, above. This article exhibits excellent cleaning of greasy/oily and particulate soils when used in the automatic washing process, and has excellent component release characteristics and a minimum of component bleeding through the substrate sheets when stored.

Component	Wt. %
$C_{17}H_{35}-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2-\overset{+}{\underset{\|}{\overset{CH_3}{\overset{\|}{N}}}}-CH_3\ Cl^-$ (CH3 below N)	21.4
Condensation product of coconut alcohol with 5 moles of ethylene oxide	42.2
Ammonia amide	5.9
Borax · 10 H_2O	10.9
Zeosyl 200	9.1
Choline Chloride	10.5

EXAMPLE VII

A substrate article of the present invention, containing the detergent composition given below, is made according to the procedure outlined in Example V, above. This article gives substantially complete release of the detergent composition from the substrates during a standard automatic laundry cycle, and exhibits minimal bleeding of the surfactant components through the substrate materials during storage. In addition, the article yields excellent cleaning of particulate and greasy/oily soils, as well as providing fabric softening, static control and dye transfer inhibition benefits to fabrics laundered with it.

Component	Wt. %
$C_{12}H_{25}-(C_2H_4O)_7-CH_2-\overset{O}{\overset{\Vert}{C}}-O-C_2H_4-\overset{+}{N}(CH_3)_3\ Cl^-$	18.3
Condensation product of coconut alcohol with 5 moles of ethylene oxide	43.7
Lauramide	4.0
Borax · 5 H_2O	10.0
Zeosyl 200	9.1
Choline chloride	10.0
Minors (suds suppressor, perfume, brightener, etc.)	balance to 100

EXAMPLE VIII

A substrate article of the present invention, containing the detergent composition given below, is formulated using the method described in Example V, above. This article exhibits both excellent release of the detergent composition during an automatic laundering operation, and a minimum of component bleeding during storage.

Component	Wt. %
Dicoconut alkyl dimethylammonium bromide	19
Condensation product of C_{14-15} alcohol with 7 moles of ethylene oxide	48
Ammonia amide	6
Bentone 27	10
Choline chloride	11
Minors (suds suppressor, perfume, brightener, etc.)	balance to 100

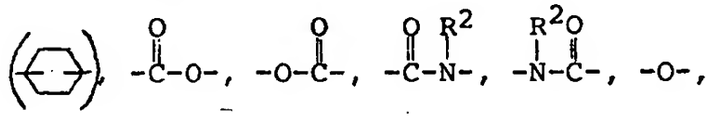
What we claim is:-

1. A laundry detergent article characterized by a water-insoluble, wet strength substrate, carrying an effective amount of a detergent composition comprising:

(a) from 5 to 95% of a surfactant mixture consisting essentially of;

(i) a nonionic surfactant having an HLB of from 5 to 17; and

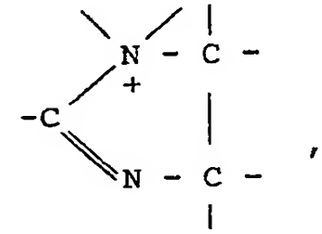
(ii) a cationic surfactant having the formula $R^1_m R^2_x Y_L Z$, wherein R^1 is an organic group containing a straight or branched alkyl or alkenyl group optionally substituted with up to 3 phenyl groups and, optionally, interrupted by up to 4 structures each of which is selected from the group consisting of



and mixtures thereof, and which contain from 8 to 22 carbon atoms, and which may additionally contain up to 20 ethoxy groups, m is a number from 1 to 7 and no more than one R^1 can have more than 12 carbon atoms when m is 3 or greater, each R^2 is an alkyl or hydroxy alkyl group containing from 1 to 4 carbon atoms or a benzyl group with no more than one R^2 in a molecule being benzyl, x is a number from 0 to 7, the remainder of any carbon, nitrogen,

sulfur or phosphorus atom positions being filled by hydrogens, Y is selected from the group consisting of:

(1)  ,

(2)  ,

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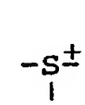
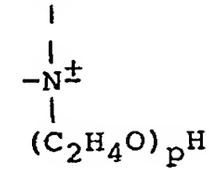
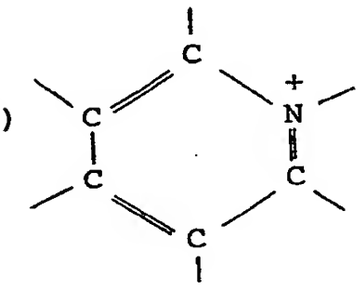
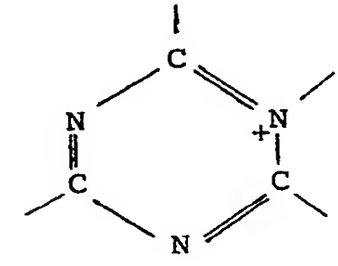
(4)  ,

(5)  wherein p is from 1 to 20,

(6)  ,

(7)  , and

(8) mixtures thereof.

L is a number from 1 to 3, Z is an anion in a number sufficient to give electrical neutrality, said cationic surfactant being at least water-dispersible in admixture with said nonionic surfactant;

the ration of said nonionic surfactant to said cationic surfactant being in the range of from 5 : 3 to 300 : 1; and

(b) from 1% to 30% of a nonionic or cationic solubilization aid which has a solubility in 100°F water of at least 20% by weight, and which completely dissolves in 100°F water in no more than 2 minutes.

2. An article according to Claim 1 characterized in that the detergent composition contains from 3% to 25% of said solubilization aid.

3. An article according to Claim 1 or 2 characterized in that said solubilization aid has a solubility in 100°F water of at least 25% by weight and completely dissolves in 100°F water in no more than one minute.

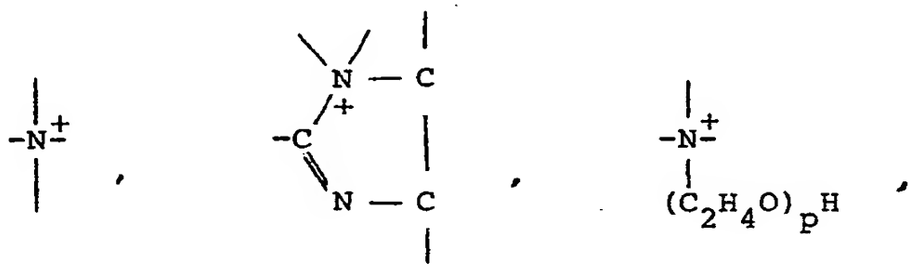
4. An article according to any preceding claim characterized in that said solubilization aid is selected from the group consisting of choline chloride, ammonium chloride, phenylmethylammonium chloride, sucrose, glucose, polyethylene glycol having a molecular weight of from about 1,000 to about 6,000 and mixtures thereof.

5. An article according to any preceding claim characterized in that said solubilization aid is hygroscopic.

6. An article according to any preceding claim characterized in that said detergent composition contains from about 10 to about 90% of the nonionic/cationic surfactant mixture, the weight ratio of nonionic surfactant to cationic surfactant being from 5 : 3 to 50 : 1.

7. An article according to any preceding claim characterized in that the nonionic surfactant has the formula $R(OC_2H_4)_nOH$, wherein R is a primary or secondary alkyl chain of from 8 to 22 carbon atoms and n is an average of from 2 to 9.

8. An article according to any preceding claim characterized in that in the cationic surfactant, L is 1, Z is an anion selected from the group consisting of halides, methylsulfate, hydroxide, and nitrate, and Y is selected from the group consisting of



and mixtures thereof.

9. An article according to any preceding claim characterized in that the detergent composition contains from 2 to 20% of an anti-bleeding material selected from the group consisting of silicas, clays, amides, soaps, and mixtures thereof, having an average particle size of no greater than 3.0 microns.

10. An arcticle according to any preceding claim characterized in that said anti-bleeding material is selected from the group consisting of silica materials having an average particle size of about 2 microns, bentonite clay materials having an average particle size of about 0.8 microns, silicate materials having an average particle size of about 1 to 2 microns, and mixtures of these materials.

11. An article according to any preceding claim wherein the substrate is selected from the group consisting of paper, woven cloth and nonwoven cloth, and carries from 3 to 120g of the detergent composition.

European Patent Office

EUROPEAN SEARCH REPORT

0002857
Application number
EP 78 200 363.6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	DE - A - 2 426 581 (COLGATE-PALMOLIVE) * page 18, example 1 * --	1
	GB - A - 1 447 448 (PROCTER AND GAMBLE) * page 8, example 1 * --	1
A	DE - A - 2 529 444 (EXQUISIT-KOSMETIK) * complete document * --	
A	DE - B - 2 106 819 (HENKEL) * complete document * ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

C 11 D 1/835
C 11 D 1/38
C 11 D 1/62
C 11 D 1/72

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

C 11 D 1/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	14-03-1979	SCHULTZE

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